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MOLECULAR ENGINEERING OF LIQUID CRYSTALLINE POLYMERS BY "LIVING"
POLYMERIZATION ~~30~~† SYNTHESIS AND "LIVING" CATIONIC POLYMERIZATION OF
(2R,3S)-2-FLUORO-3-METHYLPENTYL 4'-(8-VINYLOXYOCTYLOXY)BIPHENYL-4-
CARBOXYLATE AND ITS COPOLYMERIZATION WITH (2R,3S)-2-FLUORO-3-
METHYLPENTYL 4'-(11-VINYLOXYUNDECANYLOXY)BIPHENYL-4-CARBOXYLATE

by

V. Percec and H. Oda

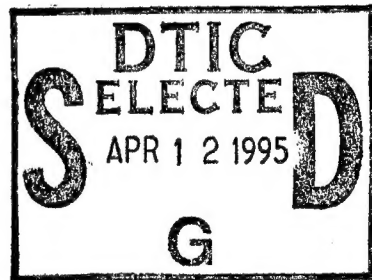
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Molecular Engineering of Liquid Crystalline Polymers by "Living" Polymerization 30.[†] Synthesis and "Living" Cationic Polymerization of (2R,3S)-2-Fluoro-3-methylpentyl 4'-(8-Vinyloxyoctyloxy)biphenyl-4-carboxylate and Its Copolymerization with (2R,3S)-2-Fluoro-3-methylpentyl 4'-(11-Vinyloxyundecanyloxy)biphenyl-4-carboxylate

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ABSTRACT

The synthesis and "living" cationic polymerization of (2R, 3S)-2-fluoro-3-methylpentyl 4'-(8-vinyloxyoctyloxy)biphenyl-4-carboxylate (**11-8**) are described. Poly(**11-8**)s with degrees of polymerization from 4.3 to 15.7 and polydispersities ≤ 1.19 were synthesized and characterized by differential scanning calorimetry (DSC) and thermal optical polarized microscopy. All poly(**11-8**)s exhibit an enantiotropic S_C^* and an unidentified smectic (S_1) phase. Poly(**11-8**)s with $DP \geq 11.5$ exhibit an additional enantiotropic unidentified smectic (S_2) phase. No S_A phase could be detected in any of poly(**11-8**)s. The nature of mesophases exhibited by poly(**11-8**) was confirmed by the investigation of the phase diagram of the copolymers prepared from **11-8** and (2R, 3S)-2-fluoro-3-methylpentyl 4'-(11-vinyloxyundecanyloxy)biphenyl-4-carboxylate (**11-11**). The S_C^* phase of these copolymers displays a continuous dependence of copolymer composition.

[†] Part 29 in this series: Ref. 1a. The definition of "living" is presented in Ref. 1b.

INTRODUCTION

Liquid crystalline polymers exhibiting chiral mesophases, such as cholesteric² and chiral smectic C (S_C^*)³ are of both theoretical and technological interest. We have performed a series of systematic investigations aimed to derive empirical rules useful for the molecular engineering of side chain liquid crystalline polymers displaying a S_C^* mesophase.⁴ In these investigations, we have used "living" cationic polymerization of mesogenic vinyl ethers for the synthesis of side chain liquid crystalline polymers. "Living" cationic polymerization can produce polymers with well defined molecular weight and narrow molecular weight distribution in the presence of a variety of functional groups and therefore, it provides access to the elucidation of the influence of molecular weight and spacer length on the formation of various mesophases.⁵

In recent years, there has been a continuing and increasing interest in the study of chiral side chain liquid crystalline polymers and a variety of polymers with new structures have been synthesized and reported.⁶⁻³⁴ Some of them show a complex phase behavior³¹⁻³³ including antiferroelectric³³ and twisted smectic A phases.³⁴

The goal of this paper is to describe the synthesis and "living" cationic polymerization of (2R, 3S)-2-fluoro-3-methylpentyl 4'-(8-vinyloxyoctyloxy)biphenyl-4-carboxylate (**11-8**) and its copolymerization with (2R, 3S)-2-fluoro-3-methylpentyl 4'-(11-vinyloxyundecanyloxy)biphenyl-4-carboxylate (**11-11**). The mesomorphic behavior of the resulting polymer poly(**11-8**) and copolymer poly[(**11-8**)-*co*-(**11-11**)] will be discussed as a function of molecular weight and copolymer composition.

EXPERIMENTAL SECTION

Materials

L-Isoleucine [(2S,3S)-(+)-2-amino-3-methylpentanoic acid, 99%], tetrabutylammonium fluoride hydrate ($n\text{-Bu}_4\text{NF}\cdot x\text{H}_2\text{O}$, 98%) and tetrabutylammonium hydrogen sulfate (TBAH, 98%) (all from Aldrich) were used as received.

NaNO_2 (Fisher) was dried at 140°C under vacuum for 40 hours before each use. Trifluoromethanesulfonic anhydride was prepared from $\text{CF}_3\text{SO}_3\text{H}$ (Lancaster, 98+%) and P_2O_5 according to a literature procedure.³⁵

Pyridine was heated overnight at 100°C over KOH, distilled from KOH, and then stored over KOH. CH_2Cl_2 was refluxed over CaH_2 overnight and distilled from CaH_2 . Dimethyl sulfoxide (DMSO) was heated overnight at 100°C over CaH_2 , distilled from CaH_2 under vacuum, and stored over molecular sieves 4\AA . Tetrahydrofuran (THF) was first distilled from LiAlH_4 and further dried over Na/benzophenone.

CH_2Cl_2 used as polymerization solvent was first washed with concentrated H_2SO_4 several times until the acid layer remained colorless, then washed with water, dried over MgSO_4 , refluxed over CaH_2 , and freshly distilled under argon before each use. $(\text{CH}_3)_2\text{S}$ used in these polymerizations (Aldrich, anhydrous, 99+%, packed under nitrogen in Sure/Seal bottle) was used as received. $\text{CF}_3\text{SO}_3\text{H}$ used as a polymerization initiator (Aldrich, 98%) was distilled under vacuum.

All other materials were commercially available and were used as received.

Techniques

^1H -NMR spectra were recorded on a Varian XL-200 (200 MHz) spectrometer.

Relative molecular weights of polymers were determined by gel permeation chromatography (GPC). GPC analyses were carried out with a Perkin-Elmer Series 10LC instrument equipped with an LC-100 column oven and a Nelson Analytical 900 Series data station. Measurements were made by using a UV detector, THF as solvent (1ml/min, 40°C), a set of PL gel columns of 5×10^2 and 10^4\AA , and a calibration plot constructed with polystyrene standards.

A Perkin-Elmer DSC-4 differential scanning calorimeter equipped with a TADS data station was used to determine the thermal transition temperatures, which were reported as the

maxima and minima of their endothermic or exothermic peaks, respectively. In all cases, heating and cooling rates were 20°C/min.

A Carl-Zeiss optical polarizing microscope equipped with a Mettler FP-82 hot stage and a Mettler FP-80 central processor was used to observe the thermal transitions and to analyze the anisotropic textures.

Synthesis of monomers

Monomers **11-8** and **11-11** were synthesized from L-isoleucine according to the reaction pathway outlined in Scheme 1. The syntheses and characterization of compounds **2** through **10-n** (n=8, 11) and of monomer **11-11** were described in detail previously.^{4,36}

(2R, 3S)-2-Fluoro-3-methylpentyl 4'-(8-Vinyloxyoctyloxy)biphenyl-4-carboxylate (11-8)

A mixture of **9** (3.70g, 11.7mmol), anhydrous K₂CO₃ (4.04g, 29.2mmol) and acetone (70ml) was stirred at 60°C under a nitrogen atmosphere for 2 h. To the resulting yellow solution was added a solution of **10-8** (2.75g, 11.7mmol) in dry DMSO (3.5ml) and stirring was continued at 60°C for 20 h. The mixture was poured into water and the product was extracted into diethyl ether twice. The combined ethereal extracts were dried over anhydrous MgSO₄. The solvent was evaporated and the remaining crude product was purified by column chromatography twice (silica gel; hexane-ethyl acetate 20:1 and 10:1) to yield a white solid (2.81g, 51.0%). Purity: >99% (HPLC). The transition temperatures (°C) are: K 44.4 S_C* 54.3 S_A 69.1 I on heating and I 64.5 S_A 50.0 S_C* 29.4 S_X 21.0 K on cooling (DSC). ¹H-NMR (CDCl₃, TMS): δ 0.97 (t, J=7.1Hz, 3H, CH₃CH₂-), 1.04 (d, J=6.8Hz, 3H, -CH(CH₃)-), 1.38 (bs, 9H, CH₃CH₂-, CH₂=CHOCH₂CH₂(CH₂)₄-), 1.55-1.75 (m, 3H, CH₃CH₂-, CH₂=CHOCH₂CH₂-), 1.75-1.97 (m, 3H, -CH(CH₃)-, -CH₂CH₂OPh-), 3.68 (t, J=6.5Hz, 2H, CH₂=CHOCH₂-), 3.98 (dd, J=6.9 and 1.9Hz, 1H, CH₂=CHO- trans), 4.01 (t, J=5.4Hz, 2H, -CH₂OPh-), 4.18 (dd, J=14.3 and 1.9Hz, 1H, CH₂=CHO- cis), 4.39-4.67, 4.79-4.93 (m, 3H, -CHFCH₂O-), 6.48 (dd, J=14.3 and 6.9Hz, 1H, CH₂=CHO-), 6.99 (d, J=8.8Hz, 2ArH, ortho to -(CH₂)₈O-), 7.57 (d, J=8.8Hz,

2ArH, meta to $-(\text{CH}_2)_8\text{O}-$), 7.64 (d, $J=8.4\text{Hz}$, 2ArH, meta to $-\text{COO}-$), 8.12 (d, $J=8.4\text{Hz}$, 2ArH, ortho to $-\text{COO}-$).

Cationic Polymerization

Polymerizations and copolymerizations were carried out in a three-necked round bottom flask equipped with a Teflon stopcock and rubber septa under an argon atmosphere at 0°C for 1 hour. All glassware was dried overnight at 140°C . The monomer was further dried under vacuum overnight in the polymerization flask. After the flask was filled with argon, freshly distilled dry CH_2Cl_2 was added via a syringe and the solution was cooled to 0°C . $(\text{CH}_3)_2\text{S}$ and $\text{CF}_3\text{SO}_3\text{H}$ were then added carefully via a syringe. The monomer concentration was about 0.224 M and the $(\text{CH}_3)_2\text{S}$ concentration was 10 times larger than that of $\text{CF}_3\text{SO}_3\text{H}$. The polymer molecular weight was controlled by the monomer/initiator ($[\text{M}]_0/[\text{I}]_0$) ratio. After quenching the polymerization with a mixture of NH_4OH and methanol (1:2), the reaction mixture was poured into methanol to give a white precipitate. The obtained polymer was purified by reprecipitation by pouring its chloroform solution into methanol, and dried under vacuum.

RESULTS AND DISCUSSION

Polymerization of **11-8**

The optical purity of monomer **11-8** was determined as reported previously³⁶ for the C2 chiral center and is 2R 96% (92% ee). As has been demonstrated previously,³⁶ no racemization takes place during the polymerization process. The optical purity derived from the C3 chiral center was not determined.³⁶

The homopolymerization of **11-8** is outlined in Scheme 2. All polymerizations were carried out at 0°C in CH_2Cl_2 by a "living" cationic polymerization technique using $\text{CF}_3\text{SO}_3\text{H}/(\text{CH}_3)_2\text{S}$ as an initiating system. Previous work in our³⁷ and other³⁸ laboratories has shown that the $\text{CF}_3\text{SO}_3\text{H}$ initiated polymerization of vinyl ethers in the presence of a Lewis base such as $(\text{CH}_3)_2\text{S}$ gives well defined polymers with controlled molecular weights and narrow

polydispersities. The polymerization mechanism is discussed in detail in previous publications.^{4,5,37}

The characterization of poly(**11-8**) by gel permeation chromatography (GPC) and differential scanning calorimetry (DSC) is summarized in Table I. The low polymer yields are the result of the loss of polymer during purification. Relative number-average molecular weights of polymers determined by GPC exhibit a linear dependence on the initial molar ratio of monomer to initiator ($[M]_0/[I]_0$) as shown in Figure 1. All polydispersities are less than 1.19. The $[M]_0/[I]_0$ ratio provides a good control of the polymer molecular weight. All these features support the typical characteristics of a "living" polymerization reaction. The absolute number-average molecular weights were difficult to determine by $^1\text{H-NMR}$ spectroscopy from the chain ends of the polymer owing to signal overlap.

The mesomorphic behavior of poly(**11-8**) was investigated by DSC and thermal optical polarized microscopy. Figures 2 presents the DSC thermograms of poly(**11-8**) with various degrees of polymerization (DP). The dependence between transition temperatures and DP is plotted in Figure 3. All virgin polymers except the one with DP=4.3 are crystalline and exhibit a crystalline melting peak on the first heating scan. However, on the subsequent cooling and heating scans all polymers exhibit enantiotropic S_C^* and S_1 (higher order smectic) mesophases. For polymers with $DP \geq 11.5$, an additional enantiotropic smectic phase (S_2) is observed in between the S_1 and S_C^* phases. The formation of the S_2 phase can be explained by the fact that the S_2 - S_C^* transition temperature has a stronger dependence on molecular weight than that of the S_1 - S_C^* transition temperature. It is interesting to note that poly(**11-8**)s do not show a S_A mesophase. Even when DSC experiments were performed at lower heating and cooling rates ($<10^\circ\text{C/min}$), the transition peak between S_C^* and isotropic phases did not split into two peaks and therefore, no evidence for the existence of the S_A phase was obtained. In the thermal microscope analysis of poly(**11-8**) with DP=11.5, for example, a focal conic texture accompanied by equidistant lines forms directly from an isotropic liquid as shown in Figures 4a and 4b. Representative textures displayed by the S_C^* and S_2 mesophases are presented in Figures 4c and

4d, respectively. The nature of the S_1 and S_2 phases was not identified. In a previous publication, we described the synthesis and "living" cationic polymerization of (R)- and (S)-2-fluoro-4-methylpentyl 4'-(8-vinyloxyoctyloxy)biphenyl-4-carboxylate (**12-8**).³⁹ The structural difference between **11-8** and **12-8** lies only in the position of the terminal methyl group as **11-8** is derived from isoleucine, while **12-8** is derived from leucine. A comparison of the phase behavior of poly(**11-8**) with that of poly(**12-8**) seems to indicate that the position of the methyl group has little effect on the phase behavior of these two polymers, since both poly(**11-8**) and poly(**12-8**) display almost identical DSC traces irrespective of their DPs. Poly(**12-8**) also did not show a S_A phase, and this was confirmed by X-ray diffraction experiments. Another similar example in which an enantiotropic S_C^* phase directly melts into and forms from an isotropic phase was reported in a previous publication from our laboratory.^{4d}

Copolymerization of **11-8** with **11-11**

The copolymerization of **11-8** with **11-11** is outlined in Scheme 3. Attempts were made to synthesize poly[(**11-8**)-*co*-(**11-11**)] with DP=20 over the entire range of compositions. The copolymerization results are summarized in Table II. The yields reported in Table II are lower than quantitative owing to the polymer loss during the purification process. However, all copolymerizations lead to almost quantitative conversions and therefore, the copolymer composition is identical to that of the monomer feed.⁵ The relative number-average molecular weight of copolymers is well controlled by the $[M]_0/[I]_0$ ratio and the molecular weight distribution of all polymers is lower than 1.13. The DSC traces of poly[(**11-8**)-*co*-(**11-11**)] are presented in Figure 5. The thermal transition temperatures determined by DSC are listed in Table II and plotted against copolymer composition in Figure 6. The mesomorphic behavior of poly(**11-11**) with various degrees of polymerization was reported in a different publication.³⁶ All poly(**11-11**)s showed enantiotropic S_A , S_C^* and unidentified higher order smectic phases regardless of their DP. The assignment of these mesophases was confirmed by a combination of thermal polarized optical microscopy and X-ray diffraction measurements. It is clear from

Figures 5 and 6 that the S_C^* mesophase displays a continuous dependence over the entire copolymer composition range. The thermal stability of the S_C^* phase is enlarged by copolymerization. The S_1 phase of poly(**11-8**) seems to be isomorphic with the higher order smectic phase of poly(**11-11**). The S_A phase in poly[(**11-8**)-*co*-(**11-11**)](X/Y) (where X/Y refers to the molar ratio of the two structural units) appears only in the range of compositions from X/Y=90/10 to 0/100 on heating and from X/Y=80/20 to 0/100 on cooling, confirming the fact that poly(**11-8**) does not exhibit a S_A mesophase. Finally, when comparing the phase behavior of poly(**11-8**) with that of poly(**11-11**), it can be concluded that a higher order mesophase is favored towards shorter spacer length. The same trend was previously reported from our laboratory in the case of polymers of (2S, 3S)-2-chloro-3-methyl 4'-(ω -vinylalkoxy)biphenyl-4-carboxylate with undecanyl, octyl and hexyl alkyl groups,^{4e,d} whose structure is identical to that of **11-n** (n=8, 11) except that the fluorine atom of **11-n** was replaced with a chlorine atom.

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SCHEME AND FIGURE CAPTIONS

Scheme 1. Synthesis of monomers **11-8** and **11-11**.

Scheme 2. Cationic polymerization of **11-8**.

Scheme 3. Cationic copolymerization of **11-8** with **11-11**.

Figure 1. Dependence of the number-average molecular weight (M_n) and polydispersity (M_w/M_n) of poly(**11-8**) determined by GPC on the $[M]_0/[I]_0$ ratio.

Figure 2. DSC thermograms (20°C/min) of poly(**11-8**) with different DP: (a) first heating scans; (b) second heating scans; (c) first cooling scans.

Figure 3. The dependence of phase transition temperatures on the degree of polymerization of poly(**11-8**): (a) data from the first heating scans; (b) data from the second heating scans; (c) data from the first cooling scans.

Figure 4. Representative optical polarized micrographs of: (a) the S_C^* mesophase displayed by poly(**11-8**) (DP=11.5) upon cooling to 109°C; (b) the S_C^* mesophase displayed by poly(**11-8**) (DP=11.5) upon cooling to 106°C; (c) the S_C^* mesophase displayed by poly(**11-8**) (DP=4.6) upon cooling to 81°C; (d) the S_2 mesophase displayed by poly(**11-8**) (DP=11.5) upon heating to 63°C.

Figure 5. DSC thermograms (20°C/min) of poly[(**11-8**)-*co*-(**11-11**)](X/Y) with different compositions: (a) first heating scans; (b) second heating scans; (c) first cooling scans.

Figure 6. The dependence of the phase transition temperatures on the composition of poly[(**11-8**)-*co*-(**11-11**)]: (a) data from the first heating scans; (b) data from the second heating scans; (c) data from the first cooling scans.

Table I. Cationic Polymerization of (2R, 3S)-2-Fluoro-3-Methylpentyl 4'-(8-Vinyloxyoctyloxy)biphenyl-4-Carboxylate (**11-8**) and Characterization of the Resulting Polymers^a

[M] ₀ /[I] ₀	Polymer Yield(%)	M _n ×10 ⁻³	M _w /M _n	DP	Phase transitions (°C) and corresponding enthalpy changes (kcal/mru) ^b	
					heating	cooling
2	42.3	2.0	1.05	4.3	S ₁ 30.8 (0.20) S _C * 87.1 (1.63) I S ₁ 31.4 (0.21) S _C * 87.7 (1.64) I	I 81.3 (-1.63) S _C * 26.8 (-0.19) S ₁
3	48.9	2.2	1.19	4.6	K 43.2 (0.64) S _C * 96.6 (1.71) I S ₁ 39.5 (0.26) S _C * 96.4 (1.60) I	I 87.8 (-1.64) S _C * 33.4 (-0.27) S ₁
5	63.6	3.4	1.09	7.3	K 52.7 (1.06) S _C * 105.5 (1.53) I S ₁ 47.9 (0.33) S _C * 106.0 (1.55) I	I 98.6 (-1.60) S _C * 42.1 (-0.35) S ₁
8	71.8	4.1	1.14	8.7	K 58.9 (1.13) S _C * 112.8 (1.64) I S ₁ 57.7 (0.64) S _C * 112.9 (1.55) I	I 104.2 (-1.52) S _C * 49.9 (-0.55) S ₁
12	83.5	5.4	1.11	11.5	K 55.9 († ^c) S ₁ 63.1 (0.75) S _C * 115.4 (1.59) I S _{X1} 63.5 (0.81) S ₂ 66.6 († ^c) S _C * 115.6 (1.54) I	I 109.2 (-1.54) S _C * 62.0 († ^c) S ₂ 58.1 (-0.69) S ₁
16	76.5	5.9	1.09	12.5	K 57.3 († ^c) S ₁ 66.5 (0.60) S ₂ 75.9 (0.02) S _C * 119.6 (1.52) I S ₁ 66.6 (0.59) S ₂ 74.3 (0.02) S _C * 119.7 (1.50) I	I 113.6 (-1.51) S _C * 69.8 (-0.03) S ₂ 61.4 (-0.52) S ₁
20	77.5	6.9	1.11	14.6	K 60.8 († ^c) S ₁ 68.8 (0.58) S ₂ 82.9 (0.06) S _C * 120.9 (1.53) I S ₁ 69.5 (0.66) S ₂ 81.9 (0.06) S _C * 120.8 (1.50) I	I 113.7 (-1.51) S _C * 76.6 (-0.06) S ₂ 62.7 (-0.55) S ₁
25	87.5	7.4	1.11	15.7	K 56.5 (0.13) S ₁ 68.1 (0.31) S ₂ 81.4 (0.02) S _C * 121.1 (1.53) I S ₁ 70.0 (0.66) S ₂ 82.9 (0.06) S _C * 121.3 (1.51) I	I 115.1 (-1.52) S _C * 78.3 (-0.05) S ₂ 63.9 (-0.56) S ₁

^a Polymerization temperature: 0°C; polymerization solvent: CH₂Cl₂; [M]₀=0.224; [Me₂S]₀/[I]₀=10; polymerization time: 1 h.

^b Heating and cooling rates are 20°C/min.

Data on the first line are from first heating and cooling scans. Data on the second line are from second heating scan.

^c Overlapped peak.

Table II. Cationic Copolymerization of **11-8** with **11-11** and Characterization of the Resulting Polymers^a

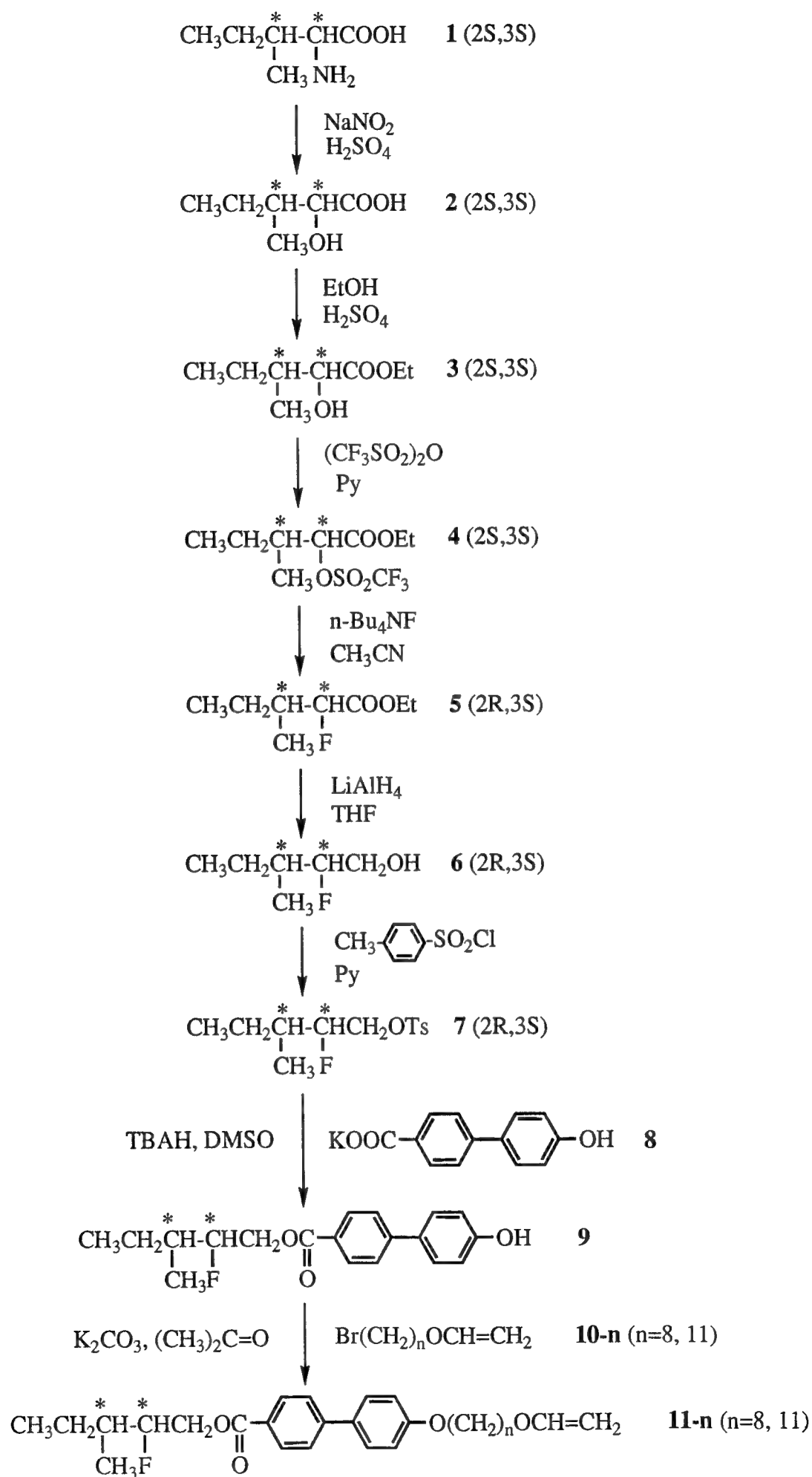
[11-8]/[11-11] (mol/mol)	Polymer Yield(%)	M _n ×10 ⁻³	M _w /M _n	DP	Phase transitions (°C) and corresponding enthalpy changes (kcal/mru) ^b	
					heating	cooling
100/0	77.5	6.9	1.11	14.6	K 60.8 († ^c) S ₁ 68.8 (0.58) S ₂ 82.9 (0.06) S _C * 120.9 (1.53) I S ₁ 69.5 (0.66) S ₂ 81.9 (0.06) S _C * 120.8 (1.50) I	I 113.7 (-1.51) S _C * 76.6 (-0.06) S ₂ 62.7 (-0.55) S ₁
90/10	77.9	6.0	1.10	12.6	K 58.5 (0.98) S ₂ 63.5 S _C * 112.3 S _A 116.4 (1.34) I S ₁ 57.6 (0.64) S ₂ 62.1 S _C * 112.3 S _A 116.2 (1.36) I	I 108.3 (-1.42) S _C * 56.6 († ^c) S ₂ 51.5 (-0.63) S ₁
80/20	84.3	6.6	1.10	13.7	K 59.2 (0.98) S ₂ 63.3 S _C * 110.2 (0.09) S _A 119.5 (1.23) I S ₁ 57.7 (0.71) S ₂ 64.0 S _C * 109.8 (0.11) S _A 119.0 (1.20) I	I 112.3 (-1.16) S _A 105.5 (-0.11) S _C * 58.2 S ₂ 52.6 (-0.67) S ₁
70/30	85.3	6.6	1.09	13.7	K 57.2 (1.08) S _C * 105.0 (0.09) S _A 119.5 (1.23) I S ₁ 55.3 (0.70) S _C * 104.6 (0.09) S _A 119.0 (1.24) I	I 111.9 (-1.21) S _A 100.0 (-0.11) S _C * 49.7 (-0.62) S ₁
60/40	80.5	6.2	1.10	12.6	K 53.9 (1.11) S _C * 97.8 (0.06) S _A 118.3 (1.30) I S ₁ 51.3 (0.64) S _C * 97.9 (0.07) S _A 117.2 (1.27) I	I 110.3 (-1.24) S _A 93.5 (-0.07) S _C * 45.6 (-0.56) S ₁
50/50	81.8	6.8	1.08	13.9	K 55.4 (1.13) S _C * 95.2 (0.06) S _A 120.6 (1.29) I S ₁ 53.2 (0.74) S _C * 94.6 (0.05) S _A 119.9 (1.28) I	I 113.0 (-1.27) S _A 90.3 (-0.06) S _C * 47.2 (-0.63) S ₁
40/60	86.3	6.3	1.13	12.8	K 54.9 (1.23) S _C * 90.4 (0.04) S _A 120.5 (1.33) I S ₁ 52.8 (0.76) S _C * 89.8 (0.04) S _A 119.7 (1.31) I	I 112.9 (-1.30) S _A 85.6 (-0.05) S _C * 46.7 (-0.67) S ₁
30/70	78.3	6.4	1.09	12.9	K 51.5 (1.17) S _C * 88.0 (0.03) S _A 119.1 (1.36) I S ₁ 50.0 (0.63) S _C * 87.4 (0.04) S _A 118.3 (1.36) I	I 111.6 (-1.35) S _A 83.2 (-0.05) S _C * 44.2 (-0.57) S ₁
20/80	84.8	6.8	1.09	13.4	K 53.8 (1.33) S _C * 88.2 (0.03) S _A 121.5 (1.38) I S ₁ 58.2 (0.71) S _C * 87.7 (0.04) S _A 120.8 (1.37) I	I 113.9 (-1.36) S _A 83.3 (-0.05) S _C * 46.9 (-0.66) S ₁
10/90	87.6	8.0	1.13	15.7	K 57.2 († ^c) S ₁ 59.1 (1.49) S _C * 90.0 (0.04) S _A 125.4 (1.37) I S ₁ 58.6 (0.94) S _C * 89.5 (0.03) S _A 124.9 (1.35) I	I 117.6 (-1.34) S _A 84.7 (-0.05) S _C * 52.3 (-0.82) S ₁
0/100	85	7.2	1.08	14.0	K 57.2 († ^c) S ₁ 60.7 (1.62) S _C * 94.5 (0.05) S _A 125.7 (1.37) I S ₁ 60.8 (1.09) S _C * 94.8 (0.04) S _A 126.1 (1.37) I	I 117.9 (-1.40) S _A 89.0 (-0.02) S _C * 53.6 (-0.94) S ₁

^a Polymerization temperature: 0°C; polymerization solvent: CH₂Cl₂; [M]₀=[**11-8**]+[**11-11**]=0.224; [M]₀/[I]₀=20; [Me₂S]₀/[I]₀=10; polymerization time: 1 h.

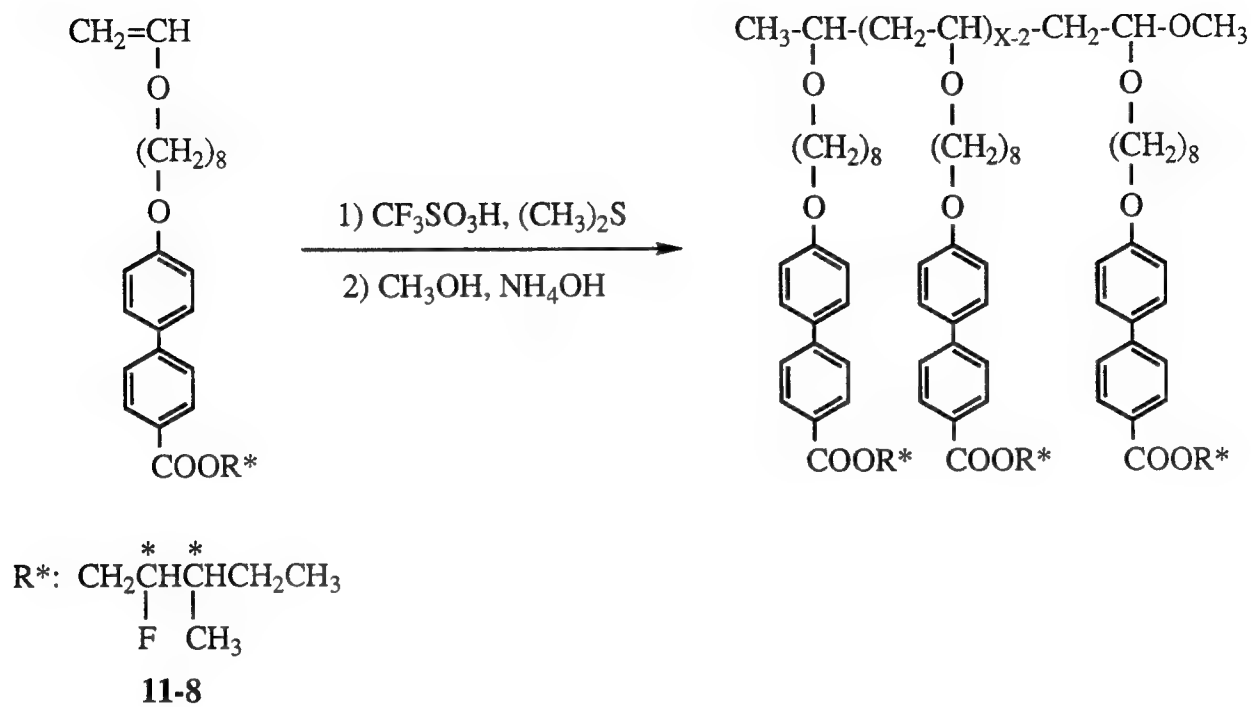
^b Heating and cooling rates are 20°C/min.

Data on the first line are from first heating and cooling scans. Data on the second line are from second heating scan.

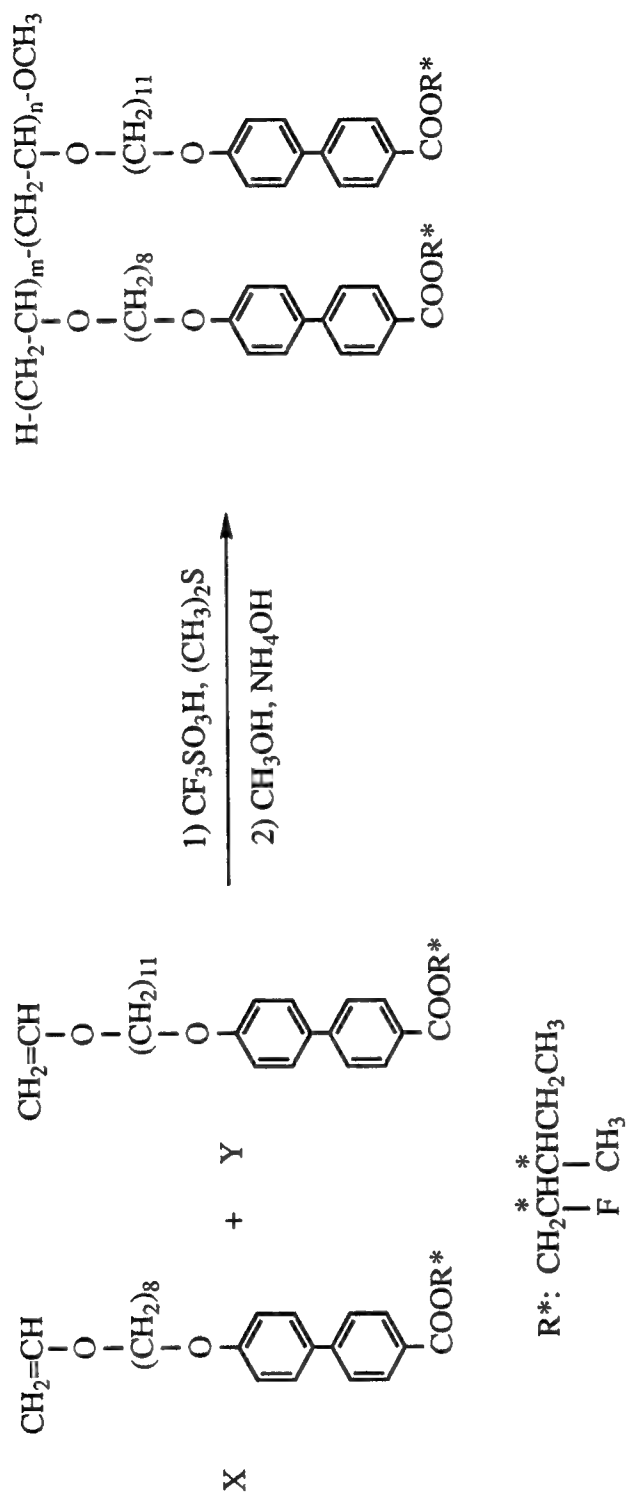
^c Overlapped peak.



Scheme 1



Scheme 2



Scheme 3

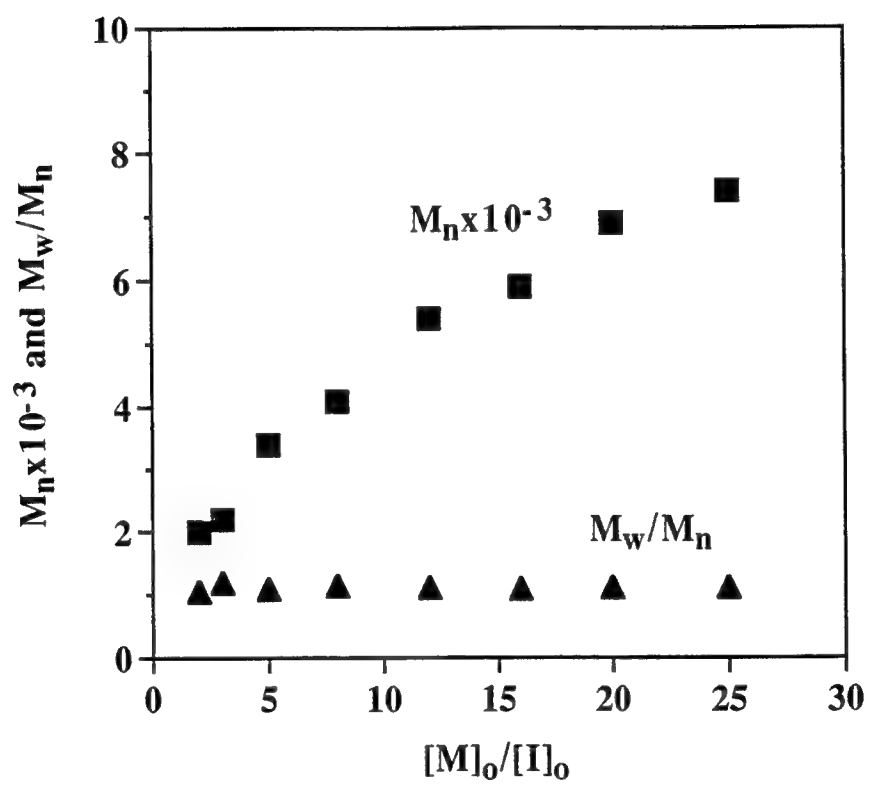


Figure 1

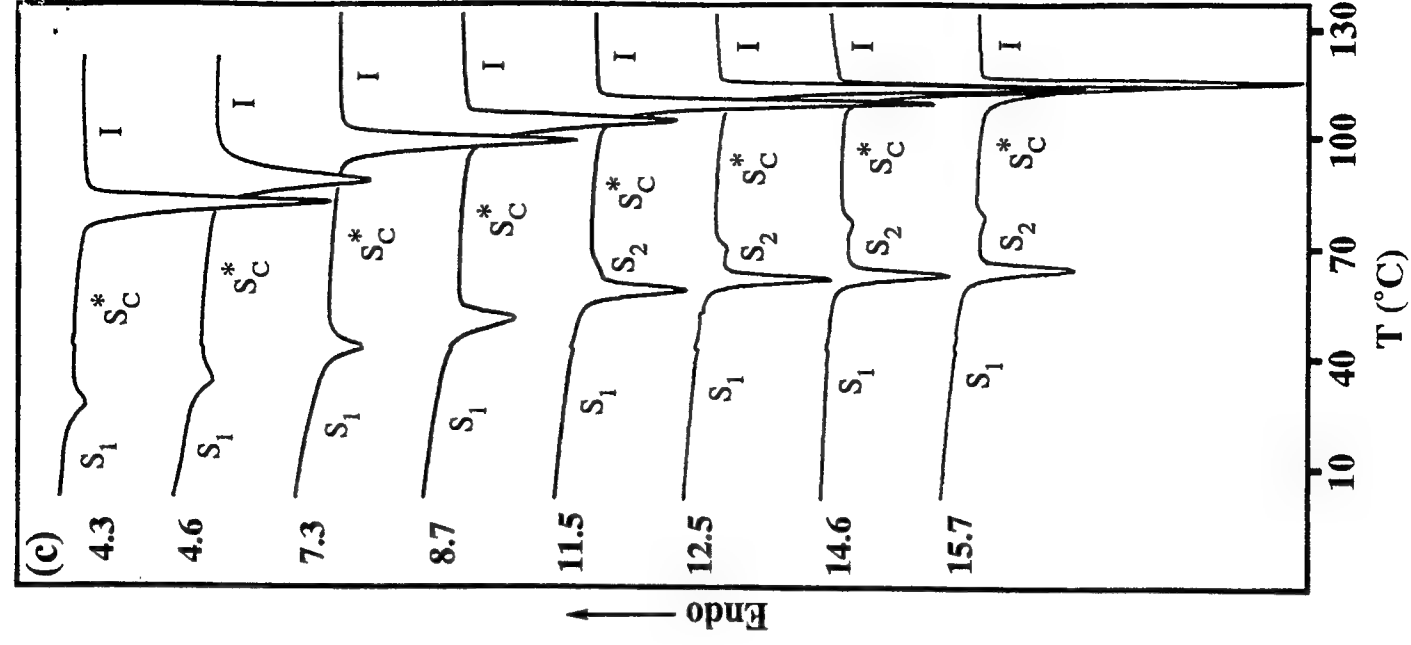
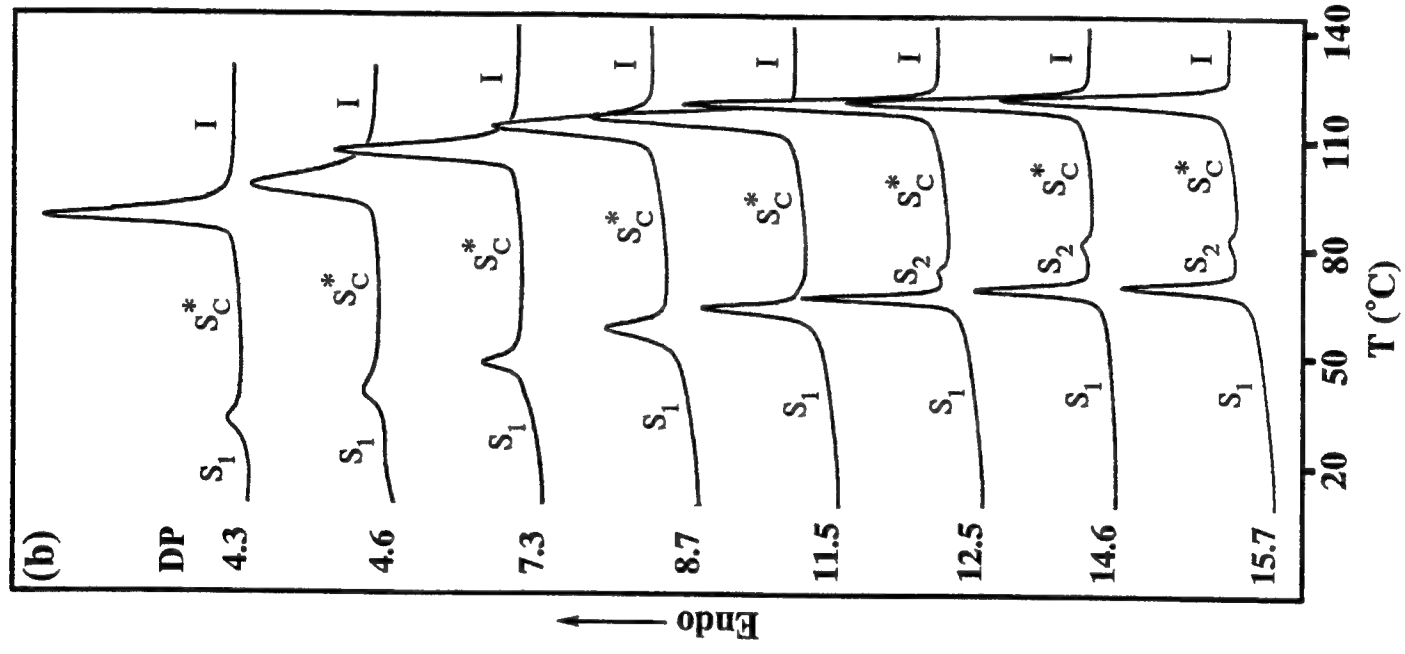
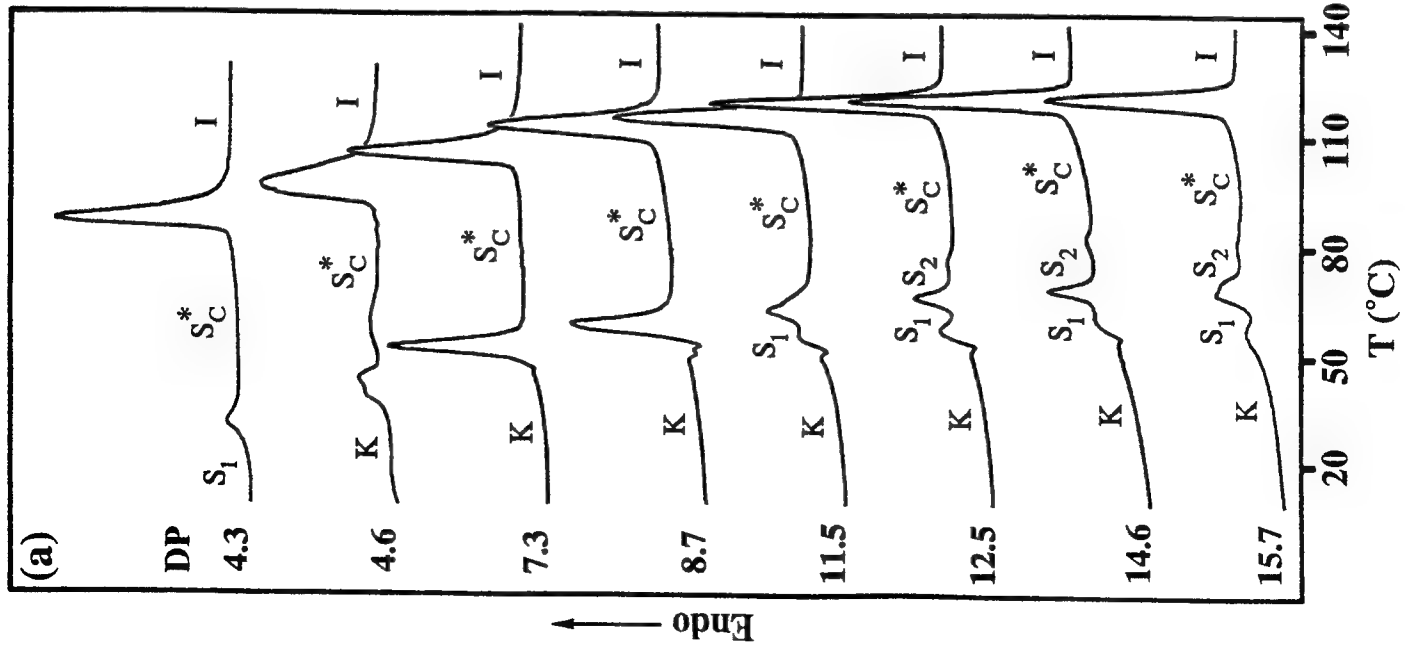


Figure 2

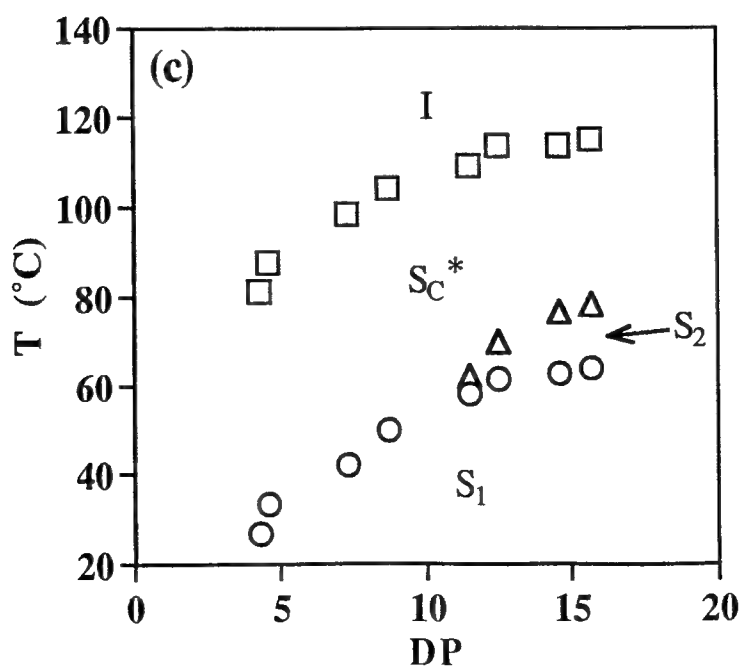
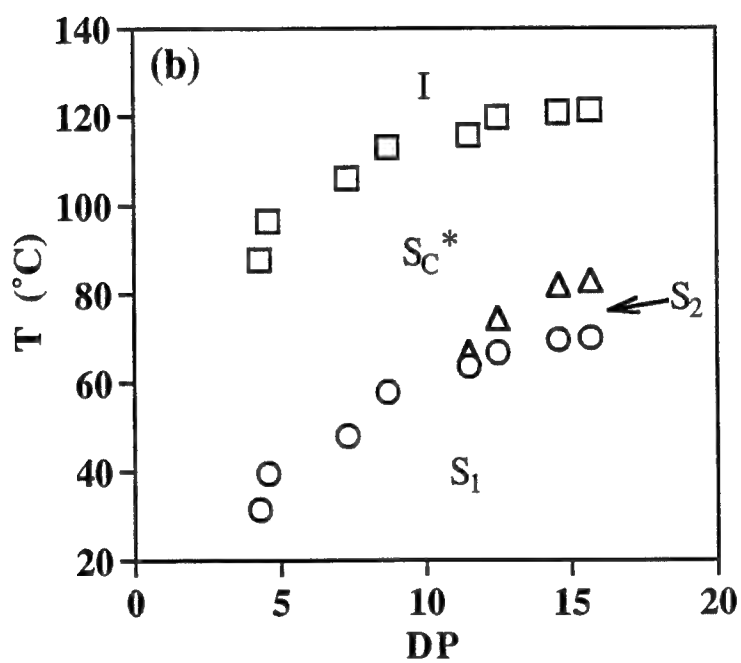
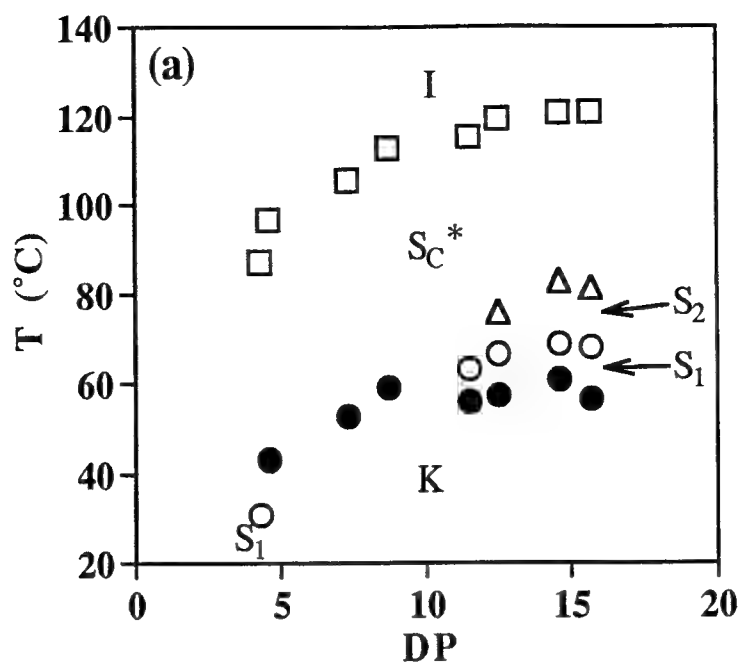
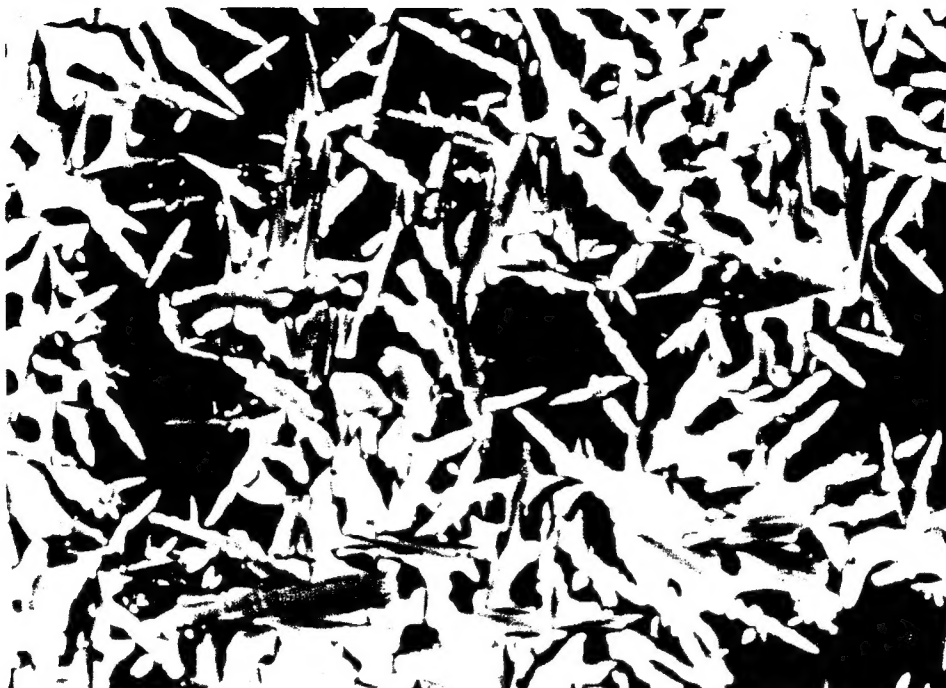


Figure 3

(a)

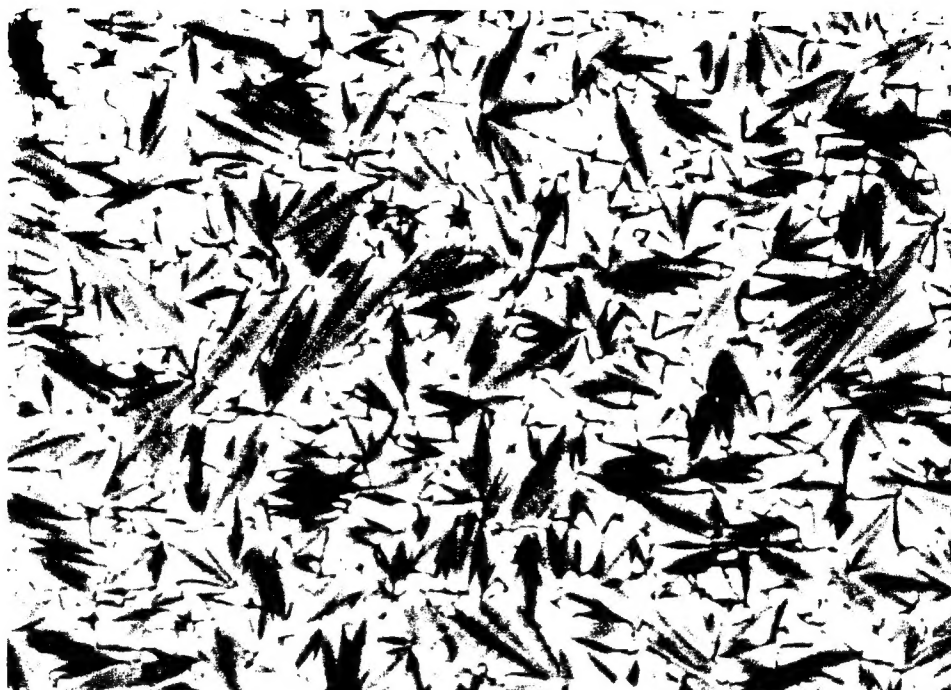


(b)



Figure 4

(c)



(d)

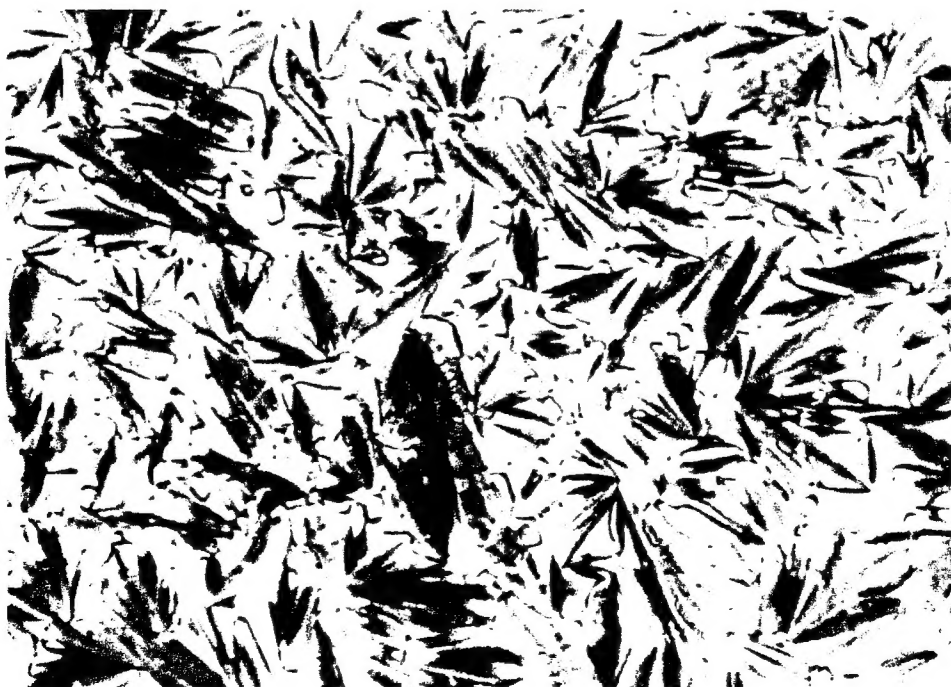


Figure 4

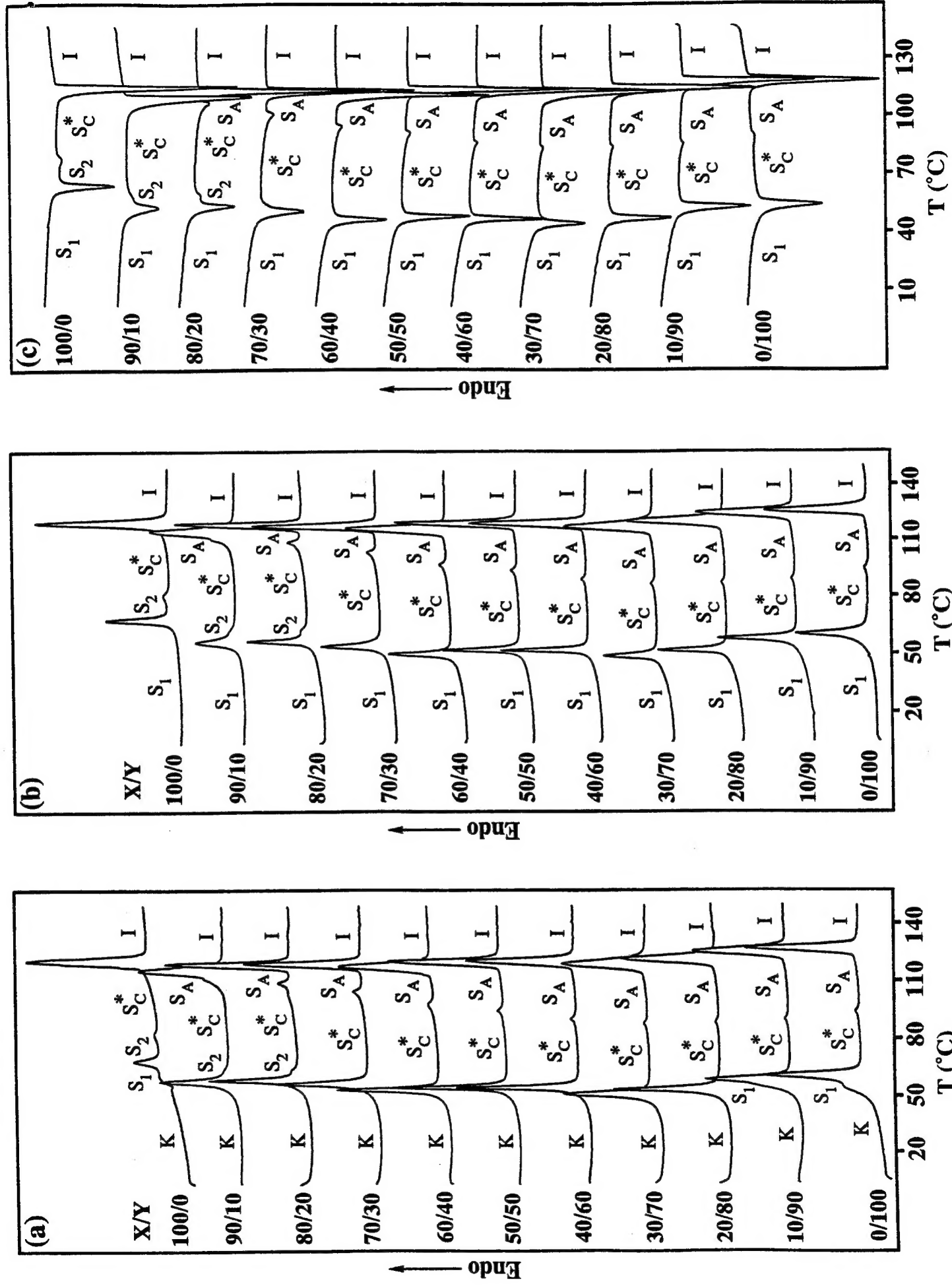


Figure 5

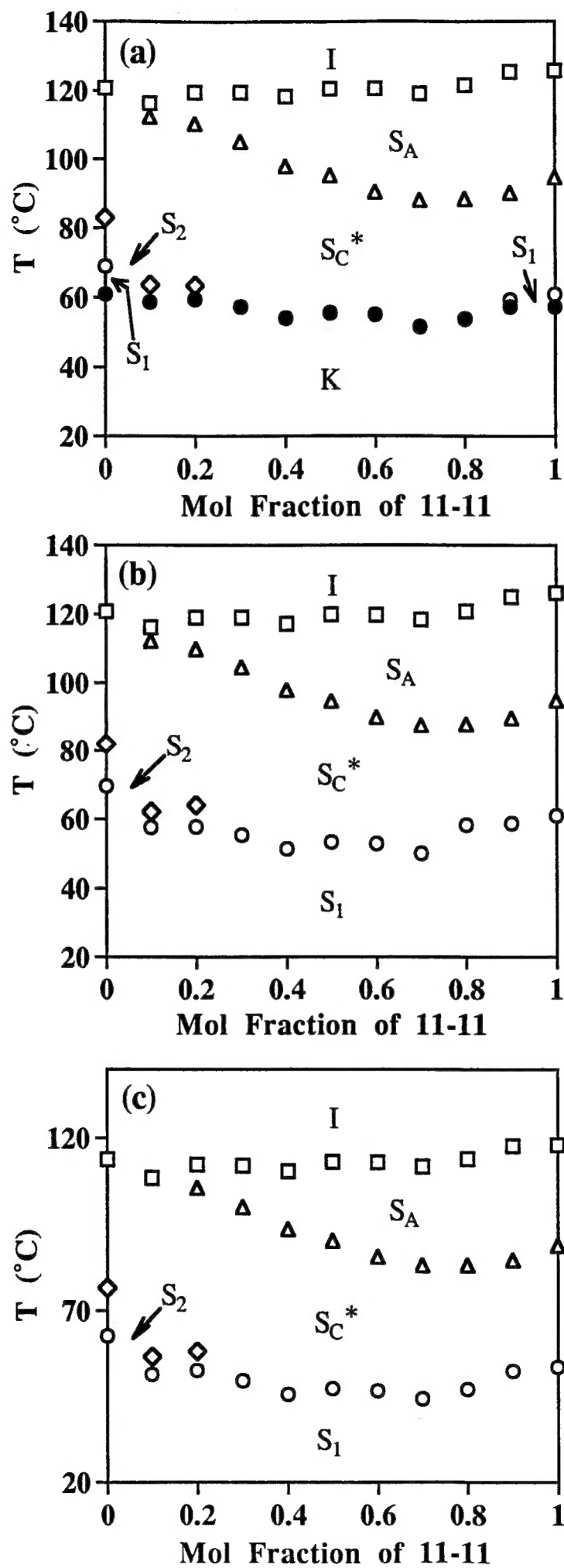


Figure 6